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Thermodynamic benchmarking of CO_2 capture systems: Exergy analysis methodology for adsorption processes

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Abstract

Exergy analyses of carbon capture systems provide a directly cross-comparable figure of merit (the exergy efficiency), and identify the process steps in each system that are most in need of improvement. In order to perform an exergy analysis of adsorption systems, the exergy of an adsorbed phase must be defined; however, the thermodynamics of these phases are different from those of bulk phases so bulk phase exergy expressions cannot be used directly. The exergy of an adsorbed phase is derived from fundamental principles. Restrictions on adsorbed-phase equations of state and mixing rules, as well as the definition of the dead state, are discussed. Examples relevant to carbon capture are presented; however, the expression derived here applies generally to adsorption processes.

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Keywords: Adsorption; exergy analysis; thermodynamic benchmarking

1. Introduction

One of the issues facing the benchmarking of CO_2 capture systems is the difficulty of cross-comparing technologies that are driven by different physical processes (e.g. absorption, cryogenic separation, mineral carbonation), with different necessary energetic inputs (e.g. compressor work, extracted steam), and at vastly different stages of technological readiness. A useful basis for comparison is to examine how each technology, in its current state of operation, compares to its own ideal operation—where ideality is limited solely by the laws of thermodynamics. This type of thermodynamic benchmarking is known as exergy analysis.

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Exergy is a thermodynamic property that quantifies the maximum amount of work that could be extracted from a resource when interacting with the environment. Because it is a measure of work *potential*, it is a quantity that can be destroyed by any real process. A process that destroys less exergy needs less exergy input (like compressor work or high-temperature steam) per unit of required product (like purified CO_2); it has a higher exergy efficiency. Because exergy is a thermodynamic property that can be defined for any sort of material or energy transfer, defining the exergy efficiency of a system provides a rigorous cross-comparable figure of merit, even for vastly different processes. Moreover, tracking the exergy destroyed through each step of a process helps set targets for that system's improvement. The process steps that destroy the most exergy are the ones that reduce the system's efficiency the most, and they are therefore the ones most in need of improvement.

Tracking the exergy destruction in a process requires a simple balance equation: The exergy destroyed in a defined system amounts to the net exergy transfer into that system, minus any accumulation of exergy inside the system. It is the accumulation term that concerns us here. Adsorption processes, whether pressure-swing (PSA), temperature-swing (TSA), or otherwise, are typically batch-cyclic processes. A significant amount of adsorption research is concerned with increasing the system efficiency by changing the nature of the steps in the batch cycle; for example, by adding extra pressure-equalization steps [1], or by including reflux steps [2]. Understanding the magnitude and location of the exergy destruction during each step directly targets problem areas for improvement. Tracking the exergy accumulated in the adsorbed phase is the critical part of this analysis. Because the thermodynamics of adsorbed phases are different from those of bulk phases, the exergy expressions for bulk phases, such as those in standard thermodynamics textbooks [3], do not apply to adsorbed phases.

In this work, we present a fully general expression for the exergy of adsorbed phases, derived from fundamental principles. The choice of equations of state and mixing rules is discussed, and examples relevant to carbon capture are presented. The underlying motivation is to bridge the gap between researchers in exergy analysis—who may be unfamiliar with the thermodynamics of adsorption processes—and adsorption researchers, who may not have exergy analysis of systems in mind when collecting data or designing new sorbents. This work is placed in the context of carbon capture systems analysis because of the timely nature of this issue and because of ongoing work by the authors in this area. However, the application of the methodology developed in this paper is not limited to this specific separation process; it can be used more generally whenever the exergy of an adsorbed phase must be calculated.

Nomenclature (SI units given as examples)

A	surface area, [m^2]
d	exact (path-independent) differential
f	fugacity, [Pa]
h	enthalpy, [J/kg]
K	Langmuir parameter, [1/Pa]
m	mass, [kg]
$\widehat{M}$	molar mass, [kg/mol]
N	amount of substance, [mol]
N_s	monolayer capacity (Langmuir parameter), [mol/kg-sorbent]
NS	total number of environmental species in the system
$NNES$	total number of non-environmental species in the system
P	pressure, [Pa]
P_i^*	standard state vapour pressure, [Pa]
Q	heat transfer, [J]
S	entropy, [J/K]
T	temperature, [K]
U	internal energy, [J]
V	volume, [m^3]
W	work, [J]
X	exergy (non-flow), [J]
x_i	adsorbed phase mole fraction

y_i	gas phase mole fraction
δ	inexact (path-dependent) differential
μ	chemical potential, [J/mol]
ν	stoichiometric coefficient
Π	spreading pressure, [Pa-m]
Φ	surface potential, [J/kg-sorbent]
Capitalization, Accents, Superscripts, and Subscripts ('X' here is a placeholder for any property)	
X	extensive property
x	intensive property
$\tilde{X}$	extensive property of the adsorbed phase, per unit mass of sorbent
$\tilde{x}$	intensive property of the adsorbed phase, per unit mass of sorbent
$\bar{x}$	partial molar property
$\hat{x}$	molar property
X^a	extensive property of the adsorbed phase
x^a	intensive property of the adsorbed phase
X^g	extensive property of the gas phase
x^g	intensive property of the gas phase
X^t	extensive property of the combined gas-sorbent-adsorbate system
x^t	intensive property of the combined gas-sorbent-adsorbate system
X^s	extensive property of the sorbent
x^s	intensive property of the sorbent
X_{gen}	generated quantity (e.g. S_{gen})
x_i	property of species *i*
x_o	property at the environmental dead state
x_{sys}	property at the system state

2. Background

2.1. Previous exergy analyses of adsorption processes

Exergy has been used as a metric, directly or indirectly, to analyze adsorption-based processes in a small number of previous studies. Banerjee et al. studied the exergy destroyed in a pressure-swing adsorption process for air separation [4], [5]. Because they were interested in overall exergy destruction in several different cycles, they could analyze the cyclic-steady-state form of their system (reached when there is no overall change in sorbent loading from one batch cycle to the next). This meant that they could treat the adsorption column as a black box, without having to quantify the exergy accumulated in the adsorbed species.

Several studies have analyzed the exergy destruction during the dehumidification of air by silica gel. Lior and Al-Sharqawi focused on the flow of humid air through a desiccant-lined channel, to understand how the transient temperature, velocity, and composition gradients at the boundary of the desiccant affected exergy destruction [6]. Because of their particular system configuration, they could treat the adsorbed-phase properties as behaving like liquid water, and account for the exergy from the heat of adsorption as a simple heat transfer. They did not need to derive a general expression for the exergy of adsorbed species.

Worek et al. tracked exergy destruction in a silica gel dehumidification batch cycle, instead of through a flowing channel [7]. This scenario bears more resemblance to the batch-cyclic processes used for carbon capture. However, they found the exergy destruction by solving for entropy generation in each cycle step, and then used the relationship between entropy generation and exergy destruction. Therefore, they did not derive an expression for the exergy of the adsorbed phase, and would not be able to track how much exergy was accumulated in any particular step, only how much was destroyed.

Kearns and Webley have been the only ones, to our knowledge, to define the exergy of an adsorbed phase explicitly instead of relying on entropy generation to perform an exergy analysis, and to do so in a way that is applicable to adsorbed mixtures of gases [8]. The system they modeled was an air separation, pressure-swing adsorption process. For this process, certain simplifications in the choice of equations of state (linear isotherms, binary mixtures, ideal gases) are valid, and were applied during their derivation. Moreover, the exergy expression they applied was taken from standard, bulk-phase thermodynamics without justification. The goal of the current work is to develop, from fundamental principles, an expression for the exergy of adsorbed phases that imposes no particular equation of state form. It should be noted that the expression derived in the current work *does* reduce to Kearns and Webley's expression when their assumptions are invoked, despite the very different approach taken in the derivation.

3. Thermodynamics of adsorption

The thermodynamics of adsorption have been studied and written about extensively, starting most notably with Gibbs in 1877 [9]. Here we summarize and discuss the results that are directly relevant to our application, namely the derivation of the exergy of adsorbed phases. For comprehensive discussion of the thermodynamics of adsorption, see the work of Young and Crowell [10], and Rudzinski and Everett [11], among others.

3.1. Definition of an adsorbed phase

In order to discuss thermodynamic properties of an adsorbed phase, we need to have a definitive sense of where and what this phase is. We can think vaguely about the "adsorbed phase" as a region near the surface of a solid where gas molecules have agglomerated at a different number density than in the bulk gas phase, as shown in Fig. 1a. However, this does not set clear boundaries between the three phases—solid (or sorbent), gas, and adsorbate. If we take an overall volume V^t that contains some solid, some bulk gas phase, and some adsorbed species, then the number density of a chemical species does not go through a detectable sharp change that would allow us to set the position of a phase boundary; the phases ease into each other. This means that it is not straightforward to split up the total volume V^t into three sub-volumes V^s, V^g, and V^a for the solid, gas, and adsorbed phases.

Gibbs [9] resolved this vagueness using a mathematical model: He introduced an artificial discontinuity—an interface—that is placed so as to account for all extensive properties of the chemical species with no loss of conserved quantities. We start with our volume V^t, which includes all three phases. Now imagine that instead of trying to create two interfaces to separate V^t into three volumes V^s, V^g, and V^a, we try instead to create a single interface between $V^{s\prime}$ and $V^{g\prime}$, as shown in Fig. 1b. Taking $V^{s\prime}$ as a property of the solid, it must have the number density of the bulk solid everywhere—it must be homogeneous, since it is a phase. Similarly, $V^{g\prime}$ should then have everywhere the number density of the bulk gas, so there will be a distinct discontinuity in particle number density at the interface between the two phases.

The number of particles in each phase, $N^{s\prime}$ and $N^{g\prime}$, will therefore vary based on the size of $V^{s\prime}$ and $V^{g\prime}$—in other words, they will vary based on the chosen position of the interface. If we are tracking a species that exists mainly in the gas phase and negligibly in the solid phase, like the example shown in Fig. 1, moving the interface to the left (into the solid) will result in a larger *total* number of particles, $N^{(g+s)\prime} = N^{g\prime}+N^{s\prime}$. Similarly, moving the interface to the right will result in a smaller number of particles $N^{(g+s)\prime}$. But the total number of particles in Fig. 1b, $N^{t\prime}$, has to be equal to the total number of particles in Fig. 1a, N^t, to ensure that matter is conserved. We can therefore think of a delta function of particle number density along the interface, accounting for the difference between N^t and $N^{t\prime}$. This difference is $N^{a\prime}$, the number of particles in the adsorbed phase, and its value will become smaller or larger as the interface is moved to the left or right, respectively.

When the expression *Gibbs dividing surface* is used, it refers to an interface that is positioned such that $N^{a\prime} = 0$, so that all particles are assigned either to the gas phase or the solid phase. This is the basis for the measurement of the void fraction of porous media: a "non-adsorbing" gas is allowed to fill a previously cleaned and evacuated sample of porous solid in a rigid tank at a set temperature and pressure. By measuring the number of moles of gas that have entered the tank to fill the sample, the volume of gas is found using an equation of state for the gas phase.

This volume is the one used to define the volumetric void fraction for the material, so this measurement effectively assigns all space either to the gas phase or to the solid phase.

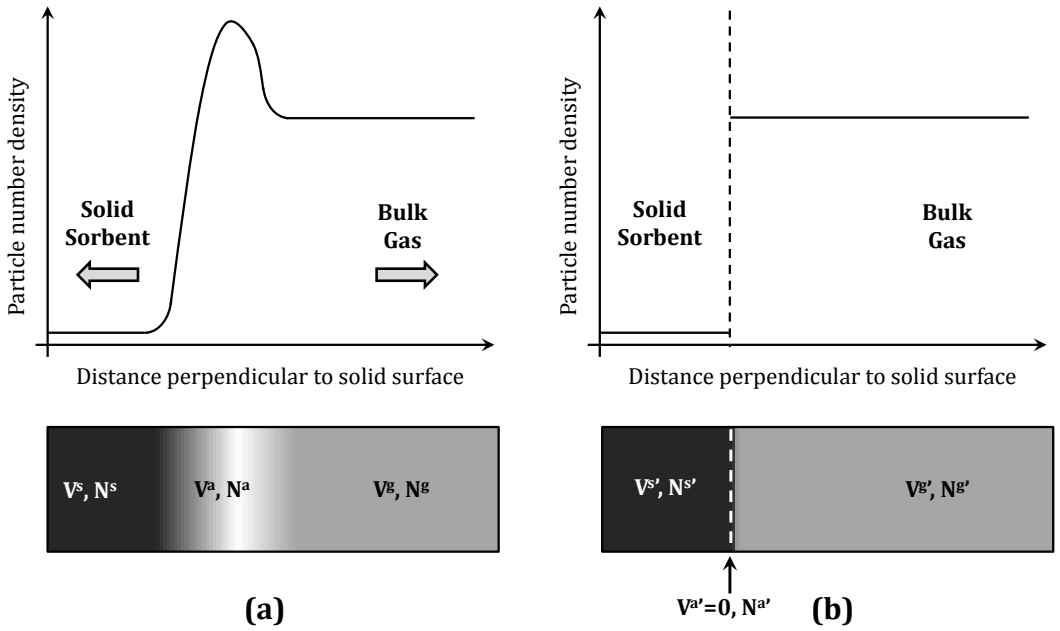

Figure 1: The gas-sorbent adsorbate interphase region, represented either by a continuous gradient (a) or by an interface (b). In each of the lower rectangles, the shading represents the particle number density represented by the plot immediately above it. Lighter shading corresponds to higher particle number density.

In actual adsorption processes, there are usually several different species present in the gas phase, which may each adsorb to different degrees. This would result in a different location for the Gibbs dividing surface for each species. In order to set a common reference, the void fraction of porous media is measured with a single component gas that is as lightly-adsorbing as possible, typically helium. This sets the position of the Gibbs dividing surface. For all other gaseous species on the same sorbent, the value of $N^{a\prime}$ is no longer zero, and there will be a delta function of particle number density at the interface. This quantity $N^{a\prime}$ is known as the *Gibbs excess adsorption*, and it determines the amount of the species that is considered to be in the adsorbed phase. The Gibbs definition of an adsorbed phase is thereby a zero-volume phase that contains the amount of species that has been assigned neither to the bulk gas phase nor to the clean, bulk solid.

3.2. Thermodynamic relations for the adsorbed phase

The discussion so far has been concerned only with defining the amount of chemical species that is assigned to the adsorbed phase. In order to define the exergy of this phase, we will also need to understand the thermodynamic relations that apply to it. The thermodynamics of these phases differ from the thermodynamics of bulk phases. Because adsorbed phases are modeled as zero-volume interfaces, the ways in which their internal energy can be modified are different from those of bulk phases. This is reflected in the adsorbed phase versions of the Gibbs equation (Eq. 1), the Euler relation (Eq. 2), and the Gibbs-Duhem equation (Eq. 3), all of which lack a pressure-volume product term. These equations can be found, with deeper discussion, in Myers [12].

Gibbs equation for adsorbed phases:

$$dU^a = TdS^a + \sum_i^{NS} \mu_i dN_i^a + \Phi dm^s \tag{1}$$

Euler relation for adsorbed phases:

$$U^a = TS^a + \sum_i^{NS} \mu_i N_i^a + \Phi m^s \tag{2}$$

Gibbs-Duhem equation for adsorbed phases:

$$m^s d\Phi = -S^a dT - \sum_i^{NS} N_i^a d\mu_i \tag{3}$$

The parameter Φ that appears in these equations is known as the surface potential, and it accounts for the change in the chemical potential of the solid sorbent as a result of adsorption. Specifically, it is the difference between the chemical potential of the clean, evacuated sorbent, and the chemical potential of the sorbent after coming to equilibrium with the adsorbed phase (on a per-mass-of-sorbent basis):

$$\Phi = \frac{1}{\widehat{M}^s}(\mu^{s,clean} - \mu^{s,post-ads}). \tag{4}$$

Even though this property originates from a change in the chemical potential of the sorbent, it is a property of the adsorbed phase under the Gibbs dividing surface concept (which assigns all adsorption-related effects, including the chemical potential change of the sorbent, to the adsorbed phase). The surface potential, Φ, is also often represented in the literature as the product of a surface area A and a spreading pressure Π, by analogy with surface tension at interfaces [12], [13], [14]. In highly porous sorbents, the surface area is often ill-defined, so the use of the surface potential Φ is preferred.

4. Exergy of the adsorbed phase

4.1. System definition

A key concept underlies the definition of the phases using the Gibbs dividing surface in Section 3: The extensive properties of the adsorbed phase are defined only by a difference between the extensive properties of an equilibrated gas-sorbent-adsorbate system and those of the free gas and clean sorbent phases. It is impossible to derive any extensive property of the adsorbed phase without starting from the extensive properties of the full, three-phase system.

For this reason, to derive the exergy of the adsorbed phase we first define a system that contains a mass m_{sys}^s of sorbent, an amount $N_{i,sys}^g$ of species i in the gas phase, and a Gibbs excess amount $N_{i,sys}^a$ of species i in the adsorbed phase. We will first derive an expression for the extensive exergy of this combined system. Then, we will solve for the exergy of the adsorbed phase by acknowledging that exergy is an extensive property, and that we can therefore subtract the exergy of the bulk gas and solid phases from the total exergy of the system:

$$X^a = X^t - (X^g + X^s), \tag{5}$$

where the superscript a refers to the adsorbed phase, g refers to the gas phase in equilibrium with that adsorbed phase, s refers to the clean solid sorbent, and t refers to the total gas-sorbent-adsorbate system.

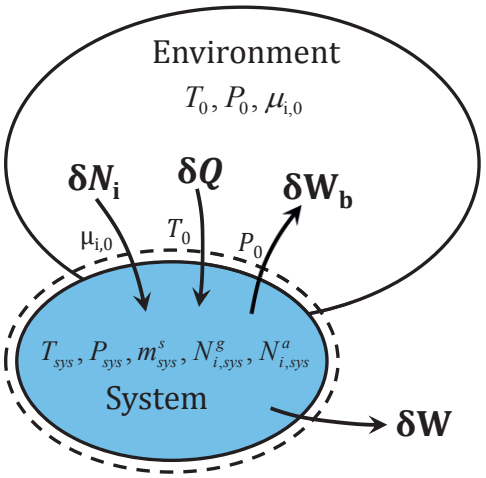

Figure 2: Definition of the system with all possible transfers. Note that the transfers cross the boundary between the system and the environment (indicated by the dashed line) at the environmental state.

The system is initially at a temperature T_{sys}, at a pressure P_{sys}, and the chemical potentials are equal across phases within the system boundary. The system is then allowed to interact with the environment, which is at a state T_o, P_o, and $\mu_{i,o}$, as shown in Fig. 2. Only three forms of interactions are possible between the system and the environment: heat transfer (δQ), matter transfer (δN_i), and boundary work (δW_b). Additionally, we allow work (δW) to be extracted from the system while it interacts with the environment. The boundary of the system, indicated by a dashed line in Fig. 2, is located such that all transfers cross the boundary at the environmental state (and any irreversibilities are confined within the system boundary). For the purpose of this derivation, positive values of δQ and δN_i represent transfers into the system, while positive values of δW_b and δW represent transfers out of the system, as indicated by the arrows in Fig. 2.

4.2. Exergy of the system

The exergy of any system is the maximum work that can be extracted while the system comes to equilibrium with the environment. Mathematically, this is defined by maximizing the path integral of δW from the system state to the environmentally equilibrated state, known as the dead state.

$$X^t = max\left(\int_{System\ State}^{Dead\ State} \delta W\right) \tag{6}$$

To find an expression for δW we start by writing balance equations for the system defined in Fig. 2.

Energy balance:

$$0 = dU^t + \delta W + \delta W_b - \delta Q - \sum_{i=1}^{NS} \bar{h}_{i,o}\delta N_i \tag{7}$$

Entropy balance:

$$\delta S_{gen} = dS^t - \frac{\delta Q}{T_o} - \sum_{i=1}^{NS} \bar{s}_{i,0}\delta N_i \tag{8}$$

In these equations, *NS* refers to the total number of chemical species, and the subscript *o* refers to the dead state. We can combine Eqs. 7 and 8 by eliminating δQ and rewriting the resulting equation to isolate δW:

$$\delta W = -dU^t - \delta W_b + T_o dS^t + \sum_{i=1}^{NS} \left(\bar{h}_{i,o} - T_o \bar{s}_{i,o}\right) \delta N_i - T_o \delta S_{gen}. \tag{9}$$

We recognize that the boundary work δW_b is given by $\delta W_b = P_o dV$ because the system boundary is located at the dead state (T_o, P_o, $\mu_{i,o}$). We also recognize that the expression $\bar{h}_{i,o} - T_o \bar{s}_{i,o}$ is the chemical potential of species *i* at the dead state, $\mu_{i,o}$. By writing the conservation law for the amount of species *i*, we know that

$$\delta \mathrm{N_i} = \mathrm{dN_i} \tag{10}$$

where δN_i refers to the transfer of species *i* from the environment to the system, while dN_i refers to the accumulation of species *i* in the system. To be able to make this equality, we have to presuppose that the adsorption process is non-reactive (i.e., that no new species are created from species in the gas phase). This comes from the definition of an adsorption process: If gas species reacted with each other on the surface, the process is catalysis, and if gas species reacted with the surface of the solid to form a new compound, it is a surface reaction. In this section, we will additionally restrict the species *i* to those that already exist in the environment. The effect of relaxing this assumption will be examined later in the paper.

Making the substitutions for boundary work, chemical potential, and transfer of species, we rewrite Eq. 9:

$$\delta W = -dU^t - P_o dV^t + T_o dS^t + \sum_{i=1}^{NS} \mu_{i.o} dN_i - T_o \delta S_{gen} \tag{11}$$

where the first four terms on the right hand side are now exact differentials and are therefore easily integrated. Integrating this expression from the system state to the resource state results in

$$\begin{aligned} \int_{System\ State}^{Dead\ State} \delta W = {} & \left(U_{sys}^t - U_o^t\right) + P_o\left(V_{sys}^t - V_o^t\right) - T_o\left(S_{sys}^t - S_o^t\right) \\ & - \sum_{i=1}^{NS} \mu_{i.o}\left(N_{i,sys}^t - N_{i,o}^t\right) - \int_{System\ State}^{Dead\ State} T_o \delta S_{gen} \end{aligned} \tag{12}$$

From Eq. 12, it is clear that the useful work extracted from the system is maximized when the process path is reversible (i.e. $S_{gen} = 0$). We therefore arrive at an expression for the exergy of the system by imposing a reversible process:

$$X^t = \left(U_{sys}^t - U_o^t\right) + P_o\left(V_{sys}^t - V_o^t\right) - T_o\left(S_{sys}^t - S_o^t\right) - \sum_{i=1}^{NS} \mu_{i.o}\left(N_{i,sys}^t - N_{i,o}^t\right). \tag{13}$$

4.3. Exergy of the adsorbed phase

The expression for the exergy of the system in Eq. 13 can be applied to any system, adsorption-related or not, under the non-reactive constraint imposed. This result is already well known (among others, [15], [16]), although the path to deriving it here is somewhat different. Showing this derivation rigorously is important for appreciating its general applicability, including to systems that include a non-negligible adsorbed phase. This approach for deriving

exergy of systems, and for the extension to non-environmental species in Section 4.7, can be seen in more detail in [18].

Expanding the terms in Eq. 13 for the gas-sorbent-adsorbate system, we can isolate the exergy of the adsorbed phase alone. For any extensive property *Z*, we know that

$$Z^t = Z^g + Z^s + Z^a \tag{14}$$

Expanding the terms in Eq. 13, we arrive at

$$\begin{aligned} X^t = &\left(U^g_{sys} + U^s_{sys} + U^a_{sys} - U^g_o - U^s_o - U^a_o\right) + P_o\left(V^g_{sys} + V^s_{sys} + V^a_{sys} - V^g_o - V^s_o - V^a_o\right) \\ &- T_o\left(S^g_{sys} + S^s_{sys} + S^a_{sys} - S^g_o - S^s_o - S^a_o\right) \\ &- \sum_{i=1}^{NS} \mu_{i.o}\left(N^g_{i,sys} + N^s_{i,sys} + N^a_{i,sys} - N^g_{i,o} - N^s_{i,o} - N^a_{i,o}\right) \end{aligned} \tag{15}$$

We can now remove the exergy of the bulk gas and sorbent phases from this combined expression. Applying Eq. 13 to the gas phase alone results in

$$X^g = \left(U^g_{sys} - U^g_o\right) + P_o\left(V^g_{sys} - V^g_o\right) - T_o\left(S^g_{sys} - S^g_o\right) - \sum_{i=1}^{NS} \mu_{i.o}\left(N^g_{i,sys} - N^g_{i,o}\right) \tag{16}$$

Here we note that we don't actually know the value of $N^g_{i,o}$ at the dead state, because an unknown amount of species *i* has left the system boundary over the course of equilibration with the environment, and an unknown amount of species *i* may have been transferred between the gas phase and the adsorbed phase during this process. However, using the Euler relation for the gas phase, we can find a relationship between the dead state quantities

$$U^g_o - T_o S^g_o + P_o V^g_o = \sum_{i}^{NS} \mu_{i,o} N^g_{i.o}, \tag{17}$$

which, when applied to Eq. 16, results in

$$X^g = U^g_{sys} + P_o V^g_{sys} - T_o S^g_{sys} - \sum_{i=1}^{NS} \mu_{i.o} N^g_{i,sys}. \tag{18}$$

The absence of extensive quantities at the dead state in Eq. 18 shows that it is not necessary to precisely know how much of species *i* has entered or left the gas phase, whether from the environment or from the adsorbed phase, during the equilibration to the dead state.

We can apply the same reasoning to the solid sorbent. This results in two equivalent expressions for the sorbent's exergy:

$$X^s = \left(U^s_{sys} - U^s_o\right) + P_o\left(V^s_{sys} - V^s_o\right) - T_o\left(S^s_{sys} - S^s_o\right) - \sum_{i=1}^{NS} \mu_{i.o}\left(N^s_{i,sys} - N^s_{i,o}\right). \tag{19}$$

$$X^s = U^s_{sys} + P_o V^s_{sys} - T_o S^s_{sys} - \sum_{i=1}^{NS} \mu_{i.o} N^s_{i,sys}. \tag{20}$$

Subtracting Eqs. 16 and 19 from Eq. 15 isolates the exergy of the adsorbed phase:

$$X^a = \left(U^a_{sys} - U^a_o\right) + P_o\left(V^a_{sys} - V^a_o\right) - T_o\left(S^a_{sys} - S^a_o\right) - \sum_{i=1}^{NS} \mu_{i.o}\left(N^a_{i,sys} - N^a_{i,o}\right) \quad (21)$$

By Gibbs' definition of an adsorbed phase, the volume of this phase is zero, whether at the system state or at the dead state, resulting in

$$X^a = \left(U^a_{sys} - U^a_o\right) - T_o\left(S^a_{sys} - S^a_o\right) - \sum_{i=1}^{NS} \mu_{i.o}\left(N^a_{i,sys} - N^a_{i,o}\right) \quad (22)$$

Finally, we can subtract the Euler relation for adsorbed phases (Eq. 2), applied at the dead state, from this expression to eliminate the extensive quantities at the dead state.

$$X^a = U^a_{sys} - T_o S^a_{sys} - \sum_{i=1}^{NS} \mu_{i.o} N^a_{i,sys} - \Phi_o m^s. \quad (23)$$

Eqs. 22 and 23 are general expressions for the exergy of the adsorbed phase. Both are equivalent, although Eq. 23 may be preferred for ease of calculation. Apart from the statement that adsorption processes are non-reactive and can be characterized using a Gibbs dividing surface, we have made no restrictions on the nature of the adsorbed phase. We have considered only environmental species so far, but this limitation will be relaxed in Section 4.7. In Sections 4.4, 4.5, and 4.6, we discuss how to calculate the thermodynamic properties of the adsorbed phase (U, S, Φ).

Kearns and Webley's final expression for the exergy of adsorption systems [8] is compatible with this result: applying their equations of state for the gas, sorbent, and adsorbed phases to Eqs. 22 or 23 results in their final expression. This compatibility can be seen as mutual reinforcement for our work and theirs. The current work justifies Kearns and Webley's initial choice of expression for exergy, and their work is an example of Eq. 22 or 23 applied to an air separation adsorption system under certain modeling assumptions.

4.4. Properties for adsorbed phases: single component

Adsorption data is usually reported along isotherms, where the amount of a species adsorbed on a given mass of sorbent is measured for a range of pressures at a constant temperature. The functional forms for these adsorption isotherms, fit to experimental data, are the thermal equations of state for adsorbed phases (analogous to the P-v-T relationships of bulk phases). With some care in the choice of the functional form, the adsorption isotherm can therefore be used to derive thermodynamic properties.

When fitting an adsorption isotherm function to a set of adsorption data, a primary concern for researchers is understandably choosing a functional form that represents the observed data's behavior well. However, the need to use the isotherm as the basis for the calculation of thermodynamic properties imposes additional restrictions.

These additional restrictions all relate to being able to solve for the surface potential Φ and its derivatives. Expressions for the surface potential, internal energy, entropy, and Gibbs free energy can be constructed from the thermodynamic relations listed in Section 3.2. Myers [17] shows these derivations in detail, and the key results are listed here in Table 1.

Table 1. Properties of single-component adsorbed species at T and P, adapted from Myers [12]. The tilde is used to indicate that the property is semi-extensive (defined per unit mass of sorbent).

Function	Symbol	Expression
Surface potential	Φ	$-RT\int_0^P \tilde{N}^a d(\ln f)$
Gibbs free energy	$\tilde{G}^a$	$\tilde{N}^a \hat{g}^g_{T,P} + \Phi$

Enthalpy	$\widetilde{H}^a$	$\widetilde{N}^a \hat{h}^g_{T,P} - T^2 \frac{\partial}{\partial T}\left[\frac{\Phi}{T}\right]_P$
Internal energy	$\widetilde{U}^a$	$\widetilde{U}^a = \widetilde{H}^a$
Entropy	$\tilde{S}^a$	$\frac{\widetilde{H}^a - \tilde{G}^a}{T}$

In order to be able to solve for the surface potential using the integral in Table 1, and then solve for all other properties of the adsorbed phase, two criteria must be satisfied. First, the adsorbed amount must be able to be defined at any T and P where state information is required. This sounds straightforward, but it is not unusual to find adsorption isotherm functional fits in the literature that are not temperature-dependent (i.e., that are fit to a single isotherm only). To be useful in a system model and exergy analysis, the adsorption isotherm should be a function of both T and P:

$$\widetilde{N}^a = \widetilde{N}^a(T, P). \tag{24}$$

The second criterion concerns the low-pressure behavior of the adsorption isotherm for the calculation of Φ. Because of the nature of the integral for Φ listed in Table 1, even small errors in the low-pressure region can cause large errors in the value of Φ. Moreover, if the functional form of the isotherm has an infinite slope at the zero pressure limits, Φ cannot be calculated. Several commonly-used isotherm forms, such as Freundlich and Sips, have this zero-pressure slope issue, and cannot be used to calculate thermodynamic properties [19].

To be useful for calculating exergy, pure component isotherms forms must also fit the experimental data's behavior well, in particular in the low pressure region. Langmuir, Toth, and UNILAN are all forms which can be used for this purpose, although the Langmuir form tends to fit experimental data less well in some regions than the latter two [20].

4.5. Properties for adsorbed phases: mixtures

There exist different approaches for finding adsorbed mixture information from pure species adsorption isotherms. For the calculation of exergy and any other thermodynamic information, it is critical that the chosen approach be thermodynamically consistent—that the Gibbs-Duhem equation for adsorbed phases (Eq. 3) be satisfied. Along an isotherm, this equation is known as the Gibbs adsorption isotherm:

$$d\Phi = -\sum_{i}^{NS} \widetilde{N}_i^a d\mu_i \tag{25}$$

The Ideal Adsorbed Solution (IAS) concept [21] provides a thermodynamically consistent framework for treating adsorbed mixtures. The procedure consists of finding, for each species *i,* a standard-state vapor pressure P_i^* such that the surface potential Φ is found to be same if calculated for each species:

$$\Phi = -RT \int_0^{P_1^*} \widetilde{N}_1^a d(\ln f) = -RT \int_0^{P_2^*} \widetilde{N}_2^a d(\ln f) = \cdots = -RT \int_0^{P_{NS}^*} \widetilde{N}_{NS}^a d(\ln f). \tag{26}$$

The quantity P_i^* is used to find adsorbed-phase mole fractions in the adsorbed-phase analog to Raoult's Law:

$$P y_i = P_i^* x_i \qquad \{i = 1,2, \ldots, NS\}. \tag{27}$$

where y_i is the gas phase mole fraction, P is the gas pressure, and x_i is the adsorbed phase mole fraction. This results in $2NS$ equations for $2NS + 1$ unknowns (P_i^*'s, x_i's, and Φ). The final equation is given by

$$1 = \sum_{i=1}^{NS} x_i. \tag{28}$$

Algorithms for solving these coupled equations are given by O'Brien and Myers [22], [23]. Once the standard-state vapor pressures are found, the properties of the adsorbed-phase mixture can be calculated, including the total amount adsorbed $N^{a,total}$ and the thermodynamic functions:

$$\frac{1}{N^{a,total}} = \sum_{i=1}^{NS} \frac{x_i}{N_i^a(T,P_i^*)} \tag{29}$$

$$\hat{u}^a(T,P,\{y_i\}) = \sum_{i=1}^{NS} x_i \hat{u}_i^a(T,P_i^*)\,, \tag{30}$$

$$\hat{s}^a(T,P,\{y_i\}) = \sum_{i=1}^{NS} x_i[\hat{s}_i^a(T,P_i^*) + R\ln x_i]. \tag{31}$$

The equations discussed here have been written for an ideal solution in the adsorbed phase (and in the gas phase). In reality, not all gas mixtures form an ideal solution in the adsorbed phase, even if they are ideal mixtures in the gas phase. The measurement, prediction, and implementation of activity coefficients for the creation of non-ideal adsorbed solutions are discussed by [19], [24], and [25] (among others).

The reason for starting from an ideal adsorbed solution, even if it does not represent all mixture well, is that it provides the correct framework for extension to non-ideal solutions—it is thermodynamically consistent. When activity coefficients are measured for the gas mixtures in the system and at the dead state, they can be incorporated into this framework. In contrast, there exist other mixing procedures for adsorption that are not always thermodynamically consistent. A commonly used one is the extended Langmuir isotherm,

$$\widetilde{N}_i^a = \frac{N_{i,s} K_i P_i}{1 + \sum_{j=1}^{NS} K_i P_j}, \tag{32}$$

where P_i represents a partial pressure, and K_i and $N_{i,s}$ are characteristic parameters of the Langmuir form. This isotherm returns the amount of species *i* adsorbed when other gases *j* are also present. It is often used due to its ease of calculation, but unless the value of $N_{i,s}$ (the monolayer capacity) is the same for all species, it is not thermodynamically consistent [26]. If used to calculate exergy, a thermodynamically inconsistent isotherm or mixing rule will return nonsensical results that can violate the second law of thermodynamics.

4.6. Definition of the dead state

The dead state is the state of mutual equilibration of a system and the environment. When the environment is large, which is generally assumed to be the case in exergy calculations, the dead state is the same as the environmental state. The dead state for bulk phases is therefore generally defined by the environmental temperature T_o, pressure P_o, and chemical potentials $\mu_{i,o}$ for each species *i* in the environment.

The same concept—that the dead state refers to the state where the system is in equilibrium with the environment—holds true for the dead state of adsorbed phases. However, unlike bulk phases, the intensive properties T, P, and μ_i are not the relevant parameters for setting the state of an adsorbed phase. Pressure is not an independent state property of adsorbed phases; it is a bulk-phase property. Instead, the state of an adsorbed phase is set by specifying the temperature T, the chemical potentials of each species μ_i, and the surface potential Φ.

Therefore, the dead state for adsorbed phases is set not by T_o, $\mu_{i,o}$, and P_o as it is for bulk phases, but instead by T_o, $\mu_{i,o}$, and Φ_o, the surface potential at the dead state.

This means that to specify the dead state for adsorption, we must know not only the temperature of the environment and the chemical potential of each environmental species, but also how each environmental species adsorbs. This involves understanding both how pure environmental species adsorb as well as how their mixtures adsorb, as explained in Sections 4.4 and 4.5.

In practice, there are very few sorbents on which the adsorption of all environmental species has been characterized. Very common sorbents, like Zeolite 13X or 5A, have been more widely studied, so this data generally exists (although, due to existing variability in sorbent nomenclature and sorbent preparation methods, data from different publications is not always cross-compatible). However, for new or specialized sorbents, a full dead state cannot be found if adsorption data does not exist for all environmental species. In this case, a "restricted" dead state (e.g. allowing the sorbent to equilibrate with the environmental compositions of known species) may be used, although this will give exergy values that differ from those where the full dead state is defined.

4.7. Adsorption of non-environmental species

In some adsorption processes, one or more of the gases being separated is a species that does not exist in the equilibrated environment. In many cases, such species can react to form environmental species. For example, methane in the environment will react with oxygen to form CO_2 and H_2O.

$$CH_4 \rightarrow CO_2 + 2H_2O - \frac{3}{2}O_2 \tag{33}$$

Placing the oxygen on the right-hand side is an intentional choice; it places all non-environmental species on the left and all environmental species on the right. We can generalize that non-environmental species (A_j) will be converted to environmental species (A_i),

$$\nu_j A_j \rightarrow \sum_{i=1}^{NS} \nu_{ij} A_i \tag{34}$$

where the ν's are signed stoichiometric coefficients. Incorporating this reaction in Eq. 10, which is the species balance for finding the total exergy of the gas-sorbent-adsorbate system, leads to

$$\delta N_i = dN_i + \sum_{j=1}^{NNES} \frac{\nu_{ij}}{\nu_j} dN_j \tag{35}$$

This equation marks the key difference between the exergy derivation restricted to environmental species, and the derivation allowing non-environmental species (that can react to become environmental species). Eq. 11 for the useful work then becomes

$$\delta W = -dU^t - P_o dV^t + T_o dS^t + \sum_{i=1}^{NS} \mu_{i.o} dN_i + \sum_{j=1}^{NNES} \mu_{i.o} \frac{\nu_{ij}}{\nu_j} dN_j - T_o \delta S_{gen} \tag{36}$$

Recognizing that $N_{j,o}^t = 0$ by the definition of a non-environmental species, Eq. 13 for the exergy of the total system becomes

$$X^t = \left(U_{sys}^t - U_o^t\right) + P_o\left(V_{sys}^t - V_o^t\right) - T_o\left(S_{sys}^t - S_o^t\right) - \sum_{i=1}^{NS} \mu_{i.o}\left(N_{i,sys}^t - N_{i,o}^t\right) - \sum_{j=1}^{NNES} \mu_{i.o} \frac{\nu_{ij}}{\nu_j} N_{j,sys}^t. \tag{37}$$

Finally, the exergy of an adsorbed phase that includes non-environmental species is given by

$$X^a = U^a_{sys} - T_o S^a_{sys} - \sum_{i=1}^{NS} \mu_{i.o} N^a_{i,sys} - \sum_{j=1}^{NNES} \mu_{i.o} \frac{\nu_{ij}}{\nu_j} N^a_{j,sys} - \Phi_o m^s. \quad (38)$$

for non-environmental species that can react to form environmental species. The extension to species that cannot react to form environmental species (mercury, for example) is possible but not treated here.

5. Illustrative examples

5.1. Exergy as a state property

Exergy is a state property of a substance and its environment. To help understand how this property behaves, the exergy of various substances is plotted in Fig. 3. The exergy of four gases is plotted as a function of pressure, for five different temperatures, on the left-hand side (Fig. 3 *a*, *c*, *e*, and *g*). These gases are, respectively, dry air (molar composition 78.08% N_2, 20.94% O_2, 0.934% Ar, and 380 ppm CO_2), pure nitrogen, pure carbon dioxide, and a representation of dry flue gas from a coal-fired power plant (molar composition 85% N_2, 15% CO_2). The dead state has the composition of dry air, a pressure of 1 bar, and a temperature of 298.15 K. The gas phase can be treated as an ideal gas for the states considered, and gas-phase properties are calculated using the Cantera open-source package for Matlab [27].

On the right-hand side (Fig. 3 *b*, *d*, *f*, and *h*) is plotted the exergy of the adsorbed phase that is in equilibrium with each of these gases on Zeolite 13X. The exergy of these gases is calculated as derived above, assuming an ideal adsorbed solution, and using pure-component adsorption isotherms from the literature. The O_2 and N_2 isotherms are taken from Baksh et al. [28]. The CO_2 isotherm is taken from Haghpanah et al. [29]. Functional forms of adsorption isotherms for argon at low pressure on Zeolite 13X are surprisingly difficult to find, but studies of air separation using this zeolite indicate that argon isotherms match oxygen closely, especially when compared to nitrogen or CO_2 [28]. For the purpose of this illustration, the argon adsorption isotherm is taken to be the same as for oxygen. The isotherms for the environmental gases at the dead state temperature are shown in Fig. 4.

Except at the dead state where it is zero, exergy is always a positive quantity, regardless of whether the system is at a higher or lower temperature, pressure, or mole fraction than the dead state. In Fig. 3, the zero-exergy state is seen in two instances: for gaseous air at 1 bar and 298.15 K, and for adsorbed air at 1 bar and 298.15 K. Note that the mole fraction of the air in the adsorbed phase will not be the same as the mole fraction of air in the gas phase. Instead, the adsorbed air has the same chemical potential as the gaseous air; the mole fractions in the adsorbed phase vary with temperature and pressure and are found using the Ideal Adsorbed Solution procedure described in Section 4.5.

For all species and phases, the value of the exergy reaches a minimum at the state that is nearest to the dead state. Mixtures that have compositions that are nearer to the dead state's have overall lower exergy. The pure nitrogen plots are only somewhat different from the air plots because air is primarily nitrogen. Similarly, the gaseous CO_2 has much larger exergy than any other species or mixture plotted because the mole fraction of CO_2 at the dead state is so low. This is well understood for the exergy of gas phases. However, the adsorbed CO_2 shows a different behavior: its exergy is considerably lower than that of the gaseous CO_2. This can be understood by noting that CO_2 adsorbs very strongly onto Zeolite 13X such that, even when in contact with 380 ppm CO_2 air, the adsorbed phase will still have a high mole fraction of CO_2. Therefore pure CO_2 adsorbed on Zeolite 13X is not nearly as different from air adsorbed on Zeolite 13X as pure CO_2 gas is from gaseous air—adsorbed CO_2's exergy is lower than that of gaseous CO_2.

A similar reasoning can be used to understand the flue gas plots. Flue gas (85% N_2, 15% CO_2) is mainly nitrogen so its gas-phase exergy, while slightly larger than that of pure nitrogen, behaves similarly. Flue gas adsorbed on Zeolite 13X, by contrast, will be much more enriched in CO_2, so this phase's exergy behaves more like pure CO_2 than like pure nitrogen.

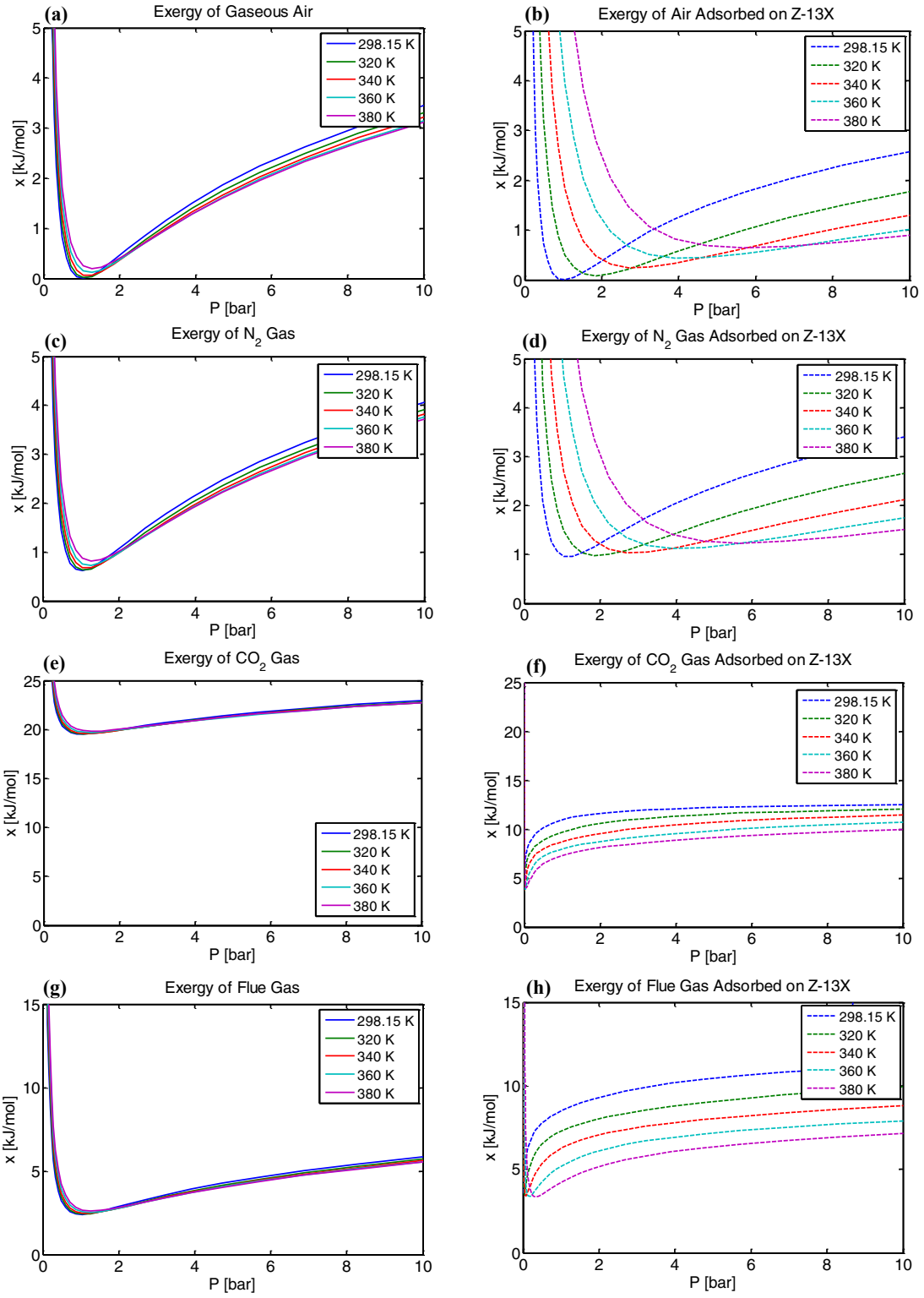

Figure 3: Exergy of various gases and gas mixtures, and exergy of the adsorbed phase in equilibrium with these gases.

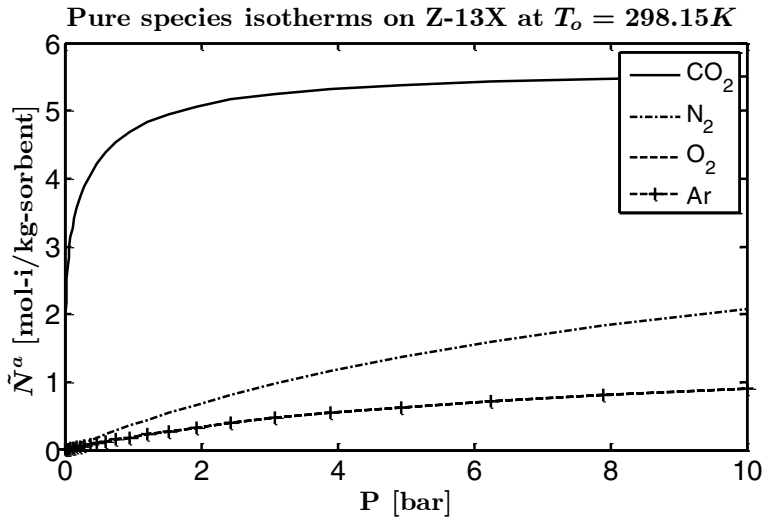

Figure 4: Adsorption isotherms on Zeolite 13X at 298.15 K, used in the calculation of dead-state properties.

6. Conclusions

This work presents the derivation, from basic principles, of the exergy of the adsorbed phase. The final result is given by Eq. 23 for cases where the adsorbed species exist in the environment, and by Eq. 38 for cases where they do not (but can react to form environmental species). During the derivation, no assumptions were made about the system's behavior, except for the validity of the Gibbs dividing surface concept to represent the adsorbed phase and the non-reactivity of the adsorbed species with the surface (and with each other). This expression can therefore be used in any adsorption process, where these assumptions hold, to track the exergy and find the locations of its destruction.

After arriving at the expression for the adsorbed-phase exergy, the restrictions for adsorbed-phase equations of state and mixing rules were discussed. Pure component adsorption isotherms must have a zero-pressure slope that is finite in order to be able to calculate the surface potential. Forming mixtures must be done in a thermodynamically consistent way, either using the Ideal Adsorbed Solution Theory directly, or using it as a framework for thermodynamically-consistent activity coefficients. The information necessary to define the dead state was discussed.

The exergy of several pure and mixed gases (air, nitrogen, CO_2, and flue gas) adsorbed on Zeolite 13X was plotted as a function of temperature and pressure, and the behavior of these plots was discussed.

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